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INVESTIGATION OF THE EXISTENCE OF OXYANIONS OF FLUORINE AND NITROGEN AND THE NITROGEN-FLUORINE CATIONS

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INVESTIGATION OF THE EXISTENCE OF OXYANIONS

OF FLUORINE AND NITROGEN AND THE NITROGEN-FLUORINE CATIONS

Summary

1. The preparation of trans-N_2F_2 from N_2F_4 and $AlCl_3$ in a flow system is described.

2. The thermal isomerization of trans-N_2F_2 to give cis-N_2F_2 must be conducted at low pressure to avoid decomposition.

3. Both cis and trans-N_2F_2 are inert to water at ambient temperatures but hydrolyze slowly at $74-90°C$ yielding mainly nitrogen, oxygen and hydrofluoric acid.

$$2N_2F_2 + 2H_2O \rightarrow 2N_2 + O_2 + 4HF$$
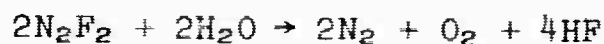
Only minor amounts of N_2O and NO_3^- are formed.

4. The hydrolytic reactions of the N_2F_2 isomers are first order with respect to the nitrogen fluorides.

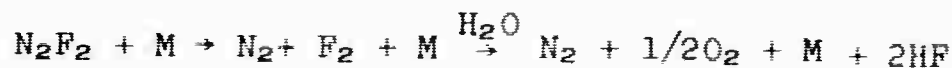5. Unlike NF_3, cis and trans-N_2F_2 are not hydrolyzed via nucleophilic attack in aqueous solution as shown by the fact that caustic soda does not significantly accelerate the reactions.

6. The mechanism of hydrolysis of cis and trans-N_2F_2 probably involves a bimolecular vapor phase decomposition reaction of the type

$$N_2F_2 + M \rightarrow N_2 + F_2 + M \overset{H_2O}{\rightarrow} N_2 + 1/2O_2 + M + 2HF$$

$$(M = \text{any molecule})$$

7. No stable intermediates are formed in the hydrolysis reactions of cis or trans-N_2F_2.

Experimental

The general experimental procedures followed in this work have been described in previous quarterly reports (HQ 76-5, 6). Details of specific experiments are given in the relevant sections of the RESULTS AND DISCUSSION section.

Mixtures of nitrogen and oxygen were frequently formed in the reactions and it was necessary to devise an analytical method suitable for determining the concentration of these gases in small samples. The following procedure was found to be convenient and sufficiently accurate:

The total amount of non-condensible gas present was determined by drawing the volatile products through liquid nitrogen-cooled traps with a Töpler pump. After establishing the absence of nitrogen fluorides or other compounds by infrared spectroscopy, a sample of the gas of known pressure and volume was weighed to establish the molecular weight and thus demonstrate the absence of hydrogen. The molecular weight bulb containing the gas at reduced pressure was opened briefly to a large volume of nitric oxide at over twice the pressure of the sample gas. The resulting mixture was allowed to stand at ambient temperature for 30 minutes to ensure completion of the reaction

$$2NO + O_2 \rightarrow 2NO_2$$
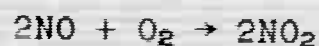
The remaining non-condensible gas (N_2) was again measured with the Töpler pump.

Because of the high volatility of nitric oxide some of this material invariably passed the liquid nitrogen traps and contaminated the nitrogen. The amount of NO present in the recovered N_2 was determined by infrared spectroscopy. It should be noted that nitric oxide is particularly susceptible to IR peak intensification as a result of pressure broadening and it is therefore necessary to measure calibration peaks at the same total pressure as that of the unknown sample. The subject of pressure broadening, especially in relation to the nitrogen fluorides, will be discussed more fully in the next quarterly report.

Preparation of trans-N_2F_2

The batch preparation of trans-N_2F_2 by the reaction of N_2F_4 with $AlCl_3$ was described in the preceding quarterly report (HQ76-6).

$$3N_2F_4 + 2AlCl_3 \rightarrow 3N_2F_2 + 3Cl_2 + 2AlF_3 \qquad I$$

This process has been adapted to small-scale flow systems with excellent results. Improved yields of N_2F_2 have been obtained from the flow reaction as compared with those previously reported for static systems (48% vs. ca. 40% based on the amount of N_2F_4 taken).

The apparatus used in the preparation of cis-N_2F_2 is shown in Figure 1. Each of the five traps (120 ml) is constructed of Pyrex glass using 160 mm sections of 18 mm tubing for the side arms. The arms of trap T_2 terminate in 18/9 ball joints to facilitate removal for cleaning and reloading with the solid reagent. Anhydrous aluminum chloride (17 g) is placed in the reaction trap T_2 and sublimed (under dry nitrogen) onto the walls of the side arm by heating the bottom of the trap with a bunsen burner. The $AlCl_3$ coating should be as evenly distributed as possible.

After connecting the trap T_2 into the reaction train the entire system is thoroughly evacuated and valves V_1, V_2, V_3 and V_4 are closed. Traps T_1, T_3, T_4 and T_5 are immersed in liquid nitrogen and trap T_2 is cooled with an acetone-CO_2 bath, which must reach above the level of the $AlCl_3$. After the desired amount of N_2F_4 (up to 50 mmoles) has been distilled into trap T_1 through valve V_1, the liquid nitrogen bath around this trap is replaced by a slush bath of methylcyclohexane or n-pentane. Valve V_2 is opened briefly to allow some N_2F_4 to pass into trap T_2. The N_2F_4 vapor should be allowed to remain in contact with the aluminum chloride for about 30 minutes in order to activate the solid and produce some elementary nitrogen. Valve V_2 is opened fully and immediately thereafter valve V_3 is opened just enough to produce a slowly increasing pressure as indicated by the "Kel-F" oil manometer. Valve V_3 should be adjusted until the pressure increases at a rate of approximately 10 mm oil/minute (1.4 mm Hg/minute). Once the flow rate

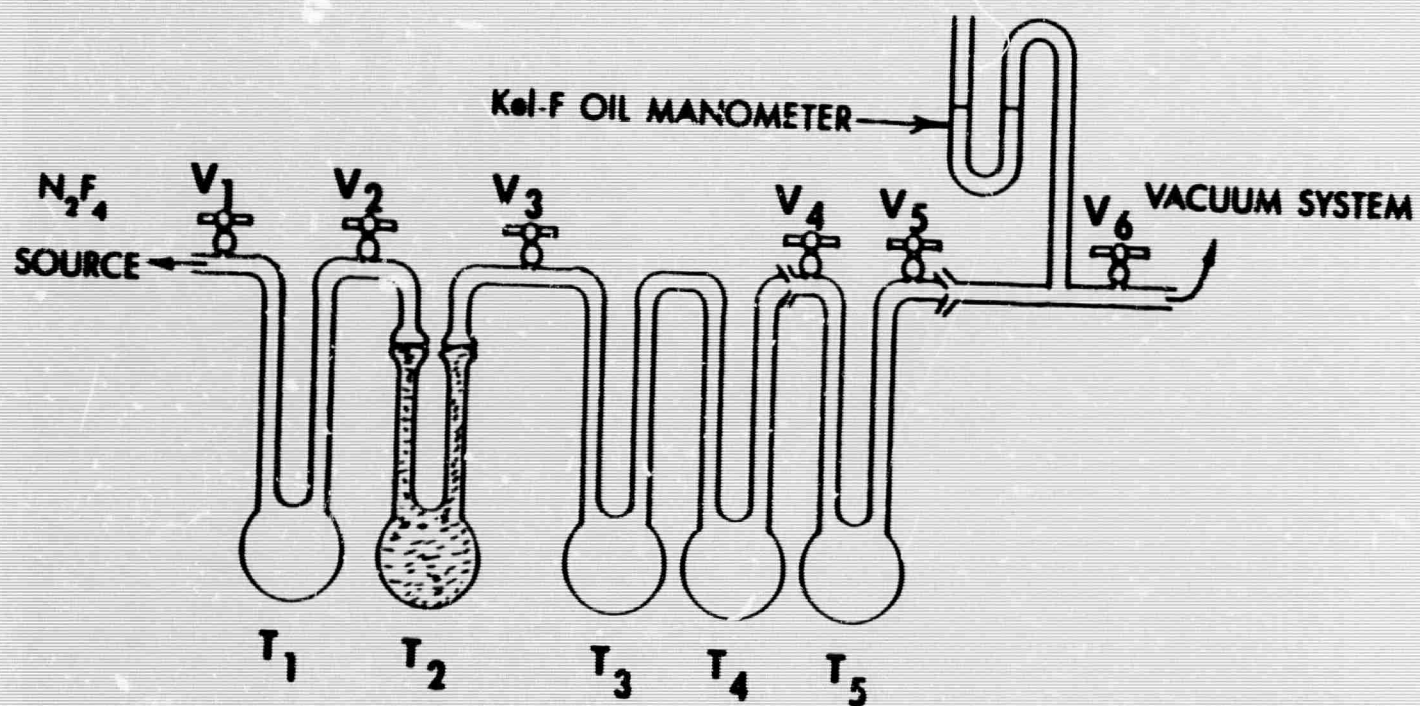# FLOW REACTOR FOR PREPARING TRANS-N_2F_2

FIGURE 1

has been established valve V_6 may be opened fully and need only be closed periodically to check the flow rate.

The reaction generates nitrogen continuously and thus the rate of escape of this gas from the reactor provides a measure of the rate at which the starting material is passing over the $AlCl_3$. It is imperative that the nitrogen be allowed to build up in trap T_2 during the activation period and that valve V_3 be opened very slowly if the rate of escape of N_2 is to be used as an indication of the flow rate of the N_2F_4.

The slush bath around trap T_1 serves to limit the pressure of the starting material to about 20 mm Hg. Obviously a mechanical pressure-reducing device may be used in place of the cooled trap T_1 and a flow meter may be substituted for the oil manometer described above. Under these conditions care should be exercized that the pressure of N_2F_4 in the reactor be kept below 20 mm Hg in order to avoid side reactions which lead to the formation of NF_3. A flow rate of approximately 10 mmoles/hour is satisfactory for a reaction tube of the approximate dimensions described above. The condensible raw product which collects in traps T_3, T_4 and T_5 (or a single trap of greater efficiency) consists mainly of a mixture of trans-N_2F_2 and chlorine along with traces of HCl and NF_3. The chlorine may be removed by vacuum distillation from a trap cooled in isopentane slush. It is recommended that the product be washed with dilute caustic soda to destroy the last traces of halogen and HCl. Any NF_3 present can be eliminated by prolonged pumping on the material at $-196°C$ or by repeated distillation of the gas into a liquid nitrogen-cooled trap open to an efficient vacuum pump.

In a typical reaction carried out as described above, N_2F_4 (17.8 mmole) from a trap cooled with methylcyclohexane was passed over $AlCl_3$ (16.7 g) over a period of 2 hours. The product was purified by trap-to-trap distillation followed by washing with water. A final distillation yielded 8.5 mmole of N_2F_2 (48%) contaminated with less than 0.2% NF_3. No other impurities were detectable in the infrared spectrum of the material at 250 mm Hg.

Isomerization of trans-N_2F_2

The thermal interconversion of the cis and trans forms of N_2F_2 has been described by Colburn et al [1].

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In each case less than 30 of the starting material was recovered and only small amounts of cis-N_2F_2 were detected. Extensive decomposition also occurred at lower temperatures (175-200°C), but only at relatively high pressures. The data in Table I vividly illustrate the effect of pressure on the amount of N_2F_2 recovered and on the yield of cis-N_2F_2. The second entry in the table represents a composite of six runs recorded immediately after the 1st entry. Only slight variations in yield were observed in the low pressure experiments.
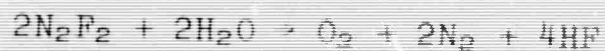
TABLE I

ISOMERIZATION OF trans-N_2F_2

Expt.	Pressure (mm)	Reaction Time (sec)	Reaction Temp. (°C)	Total N_2F_2 Recovered (%)	cis-N_2F_2 In Recovered N_2F_2 (%)
1	370	30	175-200	16	29
2-7	14-20	90	175-200	70	67

Additional work on this system is now in progress with the purpose of adapting the method to flow systems. It is anticipated that further reduction in pressure and contact time will allow the use of higher reaction temperatures and consequently increase the proportion of cis-N_2F_2 in the product.

Hydrolysis of cis and trans-N_2F_2

Few authors who have worked with difluorodiazine have failed to comment on the "vast" difference in the reactivities of the two isomers. It is therefore surprising that trans-N_2F_2 is only slightly more resistant than cis-N_2F_2 to attack by water. Both compounds are unaffected by water at 60°C over periods of 15 hours. The cis-compound hydrolyzes slowly (30% in 17 hours) at 7.°C while the trans-isomer reacts at a similar rate at 89°C. In each case the major products are nitrogen, oxygen and hydrogen fluoride.

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Nitrous oxide and NO_3^- are also formed, but only in relatively minor quantities.

The results of a number of hydrolytic experiments with cis and trans difluorodiazine are summarized in Tables II and III and Figures 2 and 3.

The data in Table II and Figure 2 were obtained by reacting samples of trans-N_2F_2 with 5 ml portions of water, aqueous NaOH (2 N) or aqueous HCl (0.5 N). The reaction vessels consisted of Pyrex ampoules (ca. 135 cc) equipped with multiple break-seals which allowed the temporary removal of volatile products at intervals during the experiments. Infrared spectroscopy was generally used in estimating the concentration of the nitrogen fluorides.

In Fig. 2 the line "A" drawn through the circled points depicts the logarithmic rate of change in the number of millimoles of trans-N_2F_2 in contact with water at 89°C as a function of time. The line "B" was obtained by plotting the function log (N_O-2/3n) against time where N_O is the initial amount of trans-N_2F_2 present and n is the total amount (millimoles) of non-condensible gas (N_2 + O_2) which had been produced in the indicated time. The linearity and nearly parallel slopes of these two lines demonstrate three significant facts:

TABLE II

HYDROLYSIS OF trans-N_2F_2 AT 89°C

Reaction	Reagent (mmoles)	Initial trans-N_2F_2 (mmoles)	Total Reaction Time (hrs)	Total Recovered trans-N_2F_2 (mmoles)	Total Products $N_2 + O_2$ (mmoles)	Other Products (mmoles)
8	H_2O (5 ml)	3.03	15.5	2.52	N_2--0.44 O_2--0.22	N_2O--0.03
			57	1.64	N_2--1.24 O_2--0.61	N_2O--0.05
			120.5	0.82	2.99	N_2O--0.06
			195.5	0.39	3.57	N_2O--0.05 NO_3^---0.02
8	2 N NaOH (5 ml)	1.41	22.5	1.10	0.47	N_2O--0.01
			118	.37	1.57	N_2O--0.03 NO_2^---0.02
10	0.5 N HCl (5 ml)	1.41	23	1.12	0.47	
			118	0.30	1.46	Cl_2--0.3

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HYDROLYSIS OF trans-N_2F_2 AT 89°C

A) trans · N_2F_2 + H_2O (5ml)

B) trans - N_2F_2 + H_2O (5ml)

ORDINATE = $N_0 - 2/3n$

where N_0 = initial N_2F_2

n = total non-condensible gas produced.

C) trans-N_2F_2 + NaOH (5ml, 2N)

D) trans-N_2F_2 + HCl (5ml, 0.5N)

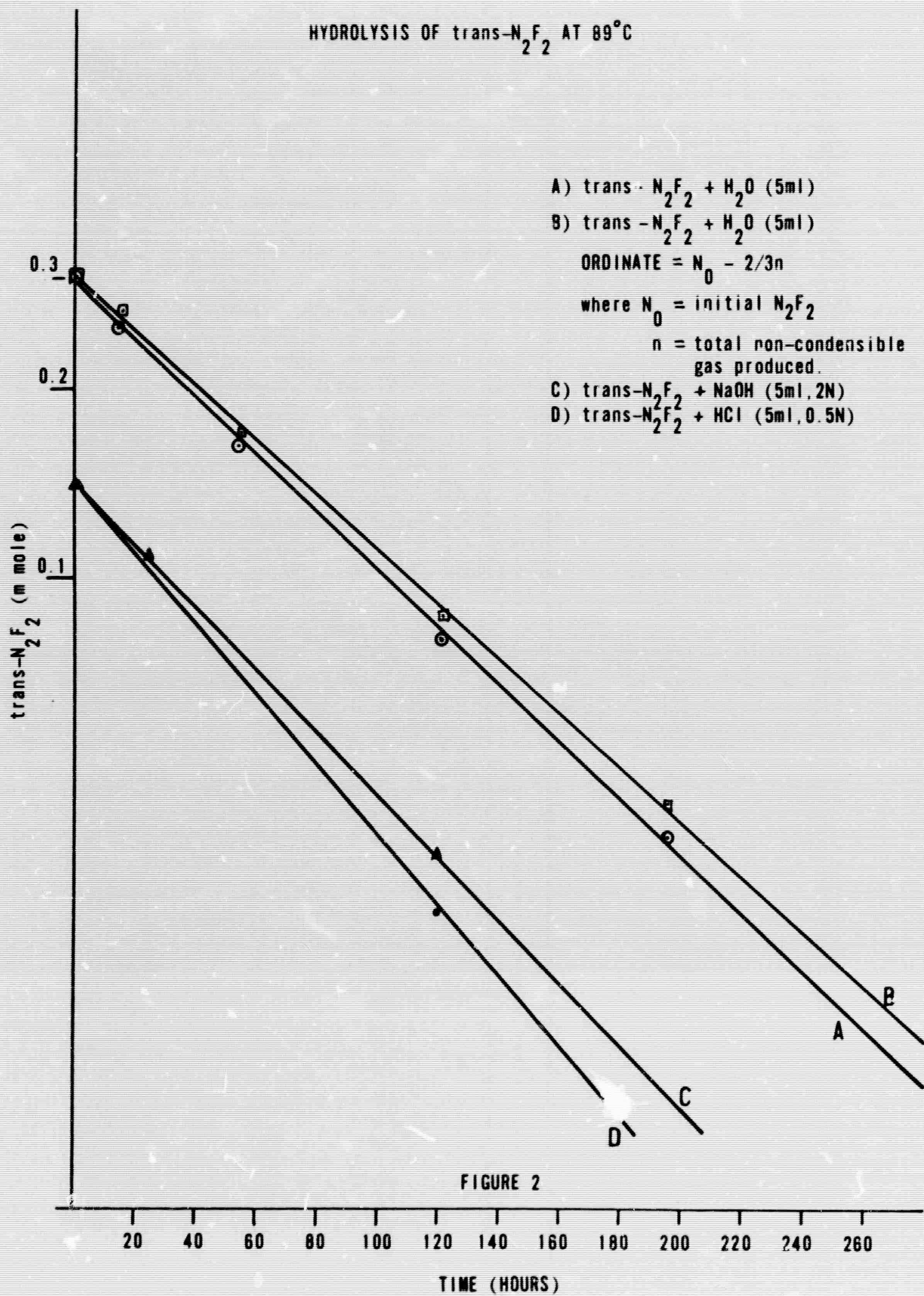trans-N_2F_2 (mmole)

FIGURE 2

TIME (HOURS)

10

TABLE III

HYDROLYSIS OF A MIXTURE OF cis AND trans-N₂F₂ AT 74°C

Reaction	Reagent	Initial N₂F₂ (mmoles)		Total Reaction Time (hrs)	Recovered N₂F₂ (mmoles)		Total Non-Cond. (mmoles)
		cis	trans		cis	trans	
11	H₂O (5 ml)	0.304	0.145	17	0.204	0.146	0.153
				32	0.132	0.139	0.246
					(.198)✿	(0.141)✿	
				50.5	0.088	0.139	0.315
				68.5	0.060	0.137	0.361
12	2 N NaOH (5 ml)	0.060	0.137	16.5	0.038	0.137	0.033

✿ Values in parentheses are actual values in mmoles that were carried forward; decrease was due to mechanical handling loss. Compensation for this loss was made in plotting the data in Fig. 3.

HYDROLYSIS OF A MIXTURE OF CIS & TRANS AT 74°C

CIS & TRANS N_2F_2 (m moles)

E) trans - N_2F_2

F) ⊙ cis - N_2F_2

□ N_0 - (2/3ṅ - Δ)

where N_0 = initial cis - N_2F_2

n = total non-condensible gas produced.

Δ = total trans - N_2F_2 reacted

( ) Points in parentheses refer to reactions with 2N NaOH in place of water.

FIGURE 3

20   40   TIME (HOURS)   60   80

12
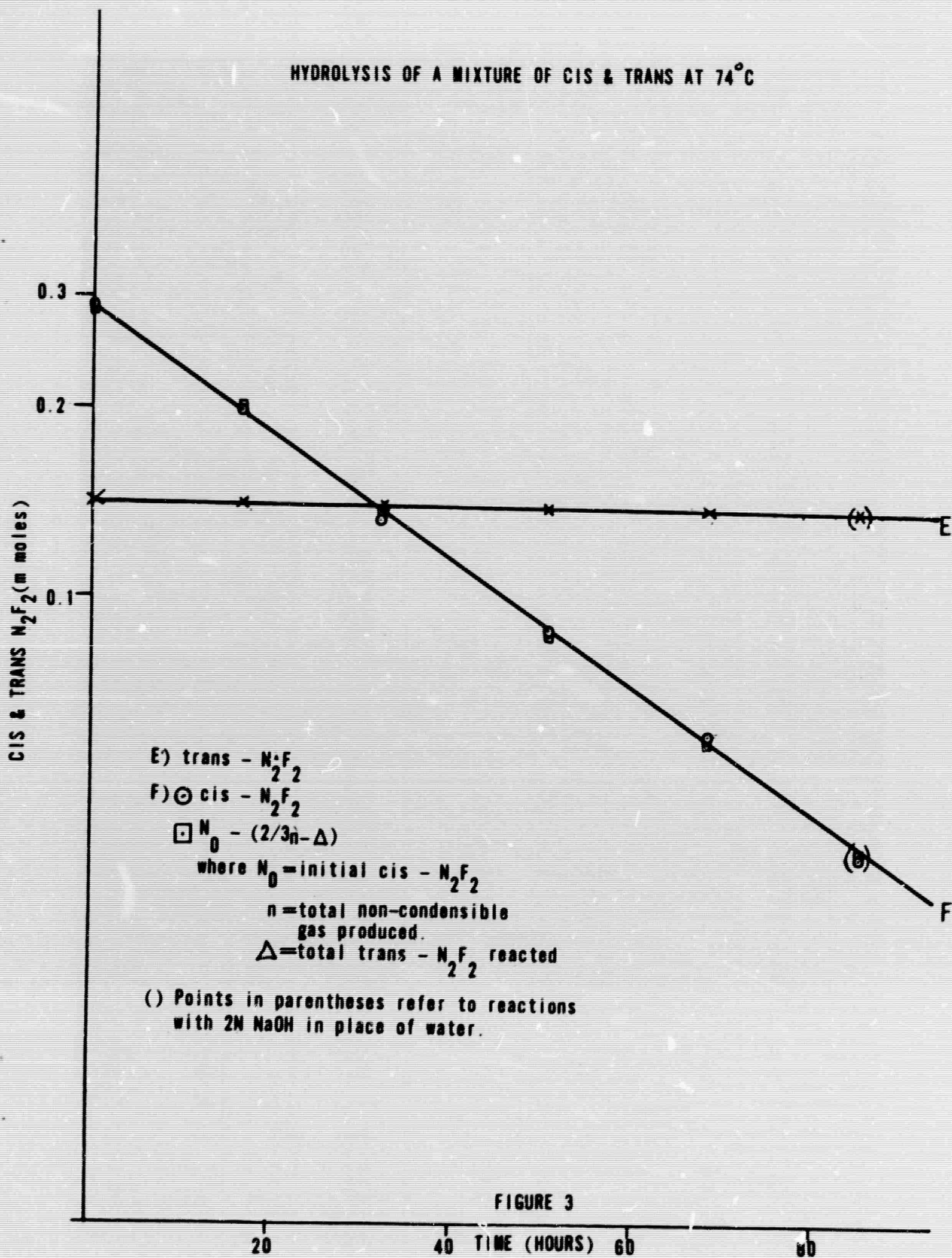
1. The reaction is first order with respect to trans-N_2F_2.

2. The stoichiometry corresponds closely to reaction IV (with the deviation at least partly due to the formation of N_2O and NO_3^-).

3. Intermediates with detectably long lifetimes are not produced.

The lines "C" and "D" were obtained from experiments involving aqueous NaOH (2 N) and aqueous HCl (0.5 N) respectively and were plotted on the same basis as line "A".

A similar set of experiments involving a mixture of cis and trans-N_2F_2 (67% cis) at 74°C is recorded in Fig. 3 and Table III. The log of the number of millimoles of the trans (line "E") and cis isomers (line "F", circled points) is again shown as a function of time. The points within the squares express the rate of formation of non-condensible gases ($N_2 + O_2$) from cis-N_2F_2 in terms of the function

$$\log \left[N_0 - (2/3\ n - \Delta) \right]$$

where N_0 is the initial amount of the cis isomer present, n is the total amount of non-condensible gas which has been produced at any time and Δ is the amount of the trans isomer reacted as given by line "E". The non-condensible function is theoretically equivalent to line "F" on the basis of reaction IV. However, the close correspondence of the two sets of data is partly fortuitous since detectable quantities of N_2O were also formed.

After the completion of the above experiments, the remaining isomeric mixture was allowed to react with 2 N NaOH (Reaction 12) under similar conditions of temperature and pressure. No change in the reaction rate or products occurred as is indicated by the points in parentheses in Fig. 3.
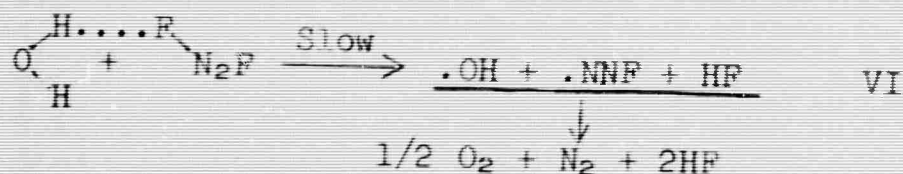
The hydrolytic behavior of N_2F_2 is anomalous as compared with that of the other binary nitrogen fluorides; nitrogen trifluoride and dinitrogen tetrafluoride both yield the corresponding oxides or oxyanions of nitrogen under mild conditions with base. This observation suggests that the mechanism of the N_2F_2 reactions is not the same as that of NF_3 or N_2F_4.

The basic hydrolysis of NF_3 has been shown to occur via nucleophilic attack in solution and there are indications that N_2F_4 behaves similarly.

$$^-HO: + N \overset{F}{\underset{\downarrow}{\diagdown}} \rightarrow HON - + F^- \\ \quad\quad\quad\quad -N=O$$
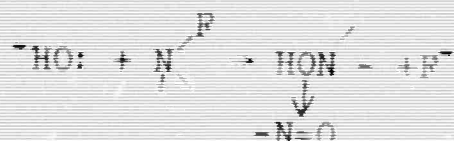
If this mechanism were involved in the hydrolysis of N_2F_2 the expected product would be N_2O. It therefore appears unlikely that nucleophilic attack is a major factor in this reaction. Additional support for this conclusion is provided by the data in Tables II and III and Figures 2 and 3 where it is shown that the rates of hydrolysis of cis and trans-N_2F_2 are first order with respect to the nitrogen fluorides and that these rates are only slightly altered in the presence of the strong nucleophile OH^-. Also in contrast to the reactions of NF_3 and N_2F_4, the rate of reaction of trans-N_2F_2 was only moderately accelerated by HCl.

The known thermodynamic instability of N_2F_2 makes it necessary to consider not only direct chemical attack by water

$$O\overset{H....F}{\underset{H}{\diagdown}} + N_2F \xrightarrow{\text{Slow}} \underline{.OH + .NNF + HF} \qquad VI \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \downarrow \\ \quad\quad\quad\quad\quad\quad\quad\quad 1/2\ O_2 + N_2 + 2HF$$

but also the thermal decomposition of the nitrogen fluoride

$$N_2F_2 \xrightarrow{\text{Slow}} N_2 + F_2 \xrightarrow{H_2O} N_2 + 1/2\ O_2 + 2HF \qquad VII$$
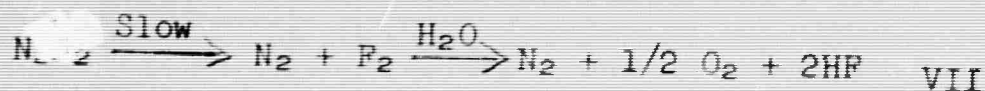
Also of interest is the possibility of competing reactions with the glass reaction vessels.

In an attempt to resolve these questions, a study was made of the non-hydrolytic decomposition of the N_2F_2 isomers. Samples of the two compounds at low pressures were heated in glass ampoules (135 ml) both alone and in the presence of nitrogen at relatively high pressure. The effect of increased glass surface area on the decomposition of trans-N_2F_2 was also investigated. The results of these experiments are summarized in Table IV.

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TABLE IV

DECOMPOSITION OF cis AND trans-N₂F₂ IN GLASS

Initial N₂F₂ (mmole)	Initial Partial Pressure Of N₂F₂ At Reaction Temp. (mm Hg)	Partial Pressure Of N₂ (mm Hg)	Surface Area / Volume cm⁻¹	Reaction Temp. (°C)	Time (?)	Decomposition
trans (0.240)	40	500	1.8	89	18	9
trans (0.246)	40	500	1.8	89	16	11
trans (0.229)	40	nil	1.8	89	16	5
trans (0.217)	36	nil	1.9	89	18	5
trans (0.412)	69	nil	1.8	89	16	5
trans (0.412)	69	500	1.9	89	16	10
trans (.040)	67	500	6.7	89	16.5	11
cis (.028) trans (.137)	cis (6) trans (29)	300	1.9	75	18	cis (15) trans (nil)
cis (0.024) trans (0.437)	cis (5.1) trans (29)	nil	1.9	75	18	cis (8) trans (nil)
*trans (0.246)	-	500	1.8	-	-	nil

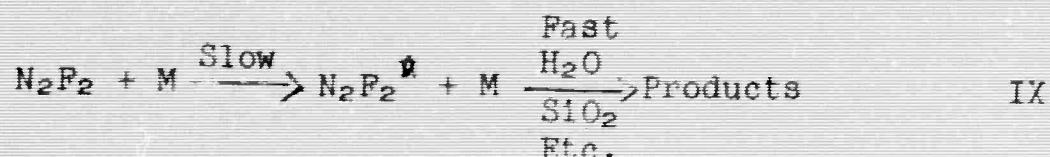* Control run to establish efficiency of recovery technique.

The data in Table IV show that pure trans-N_2F_2 decomposes slowly in glass at 89°C under low pressure and that the rate tends to increase in the presence of an excess of inert gas; a similar accelerating effect occurs with the cis isomer at 74°C. The reaction under nitrogen apparently does not involve attack on glass by (unactivated) trans-N_2F_2 since the rate was essentially unaffected by a large increase in the surface area of the reactor. The corresponding surface area data for the cis isomer have not yet been obtained. The extent of decomposition of cis and trans-N_2F_2 with nitrogen was approximately half that recorded for reactions involving an equivalent vapor pressure of water.

In view of the above evidence it must be concluded that the reactions of cis and trans-N_2F_2 cannot adequately be described in terms of simple hydrolytic attack. The fact that water is more effective than nitrogen in decomposing N_2F_2 may be the result of a contributing hydrolytic mechanism such as VI, but it is equally possible that the water molecule merely acts as a more efficient physical agent in promoting the decomposition. In this connection it should be noted that nitric oxide was found to be more than twice as active as water in destroying trans N_2F_2. On the basis of these observations, the hydrolysis of the isomers may best be written in the form

$$N_2F_2 + H_2O + M \rightarrow N_2 + 1/2\ O_2 + 2HF + M \qquad\qquad VIII$$

where M is any gaseous molecule.

Unfortunately the kinetic measurements do not provide data which can be used to differentiate between decomposition to the elements and the formation of an activated intermediate as the rate-determining step.

$$N_2F_2 + M \xrightarrow{\text{Slow}} N_2F_2^* + M \xrightarrow[\substack{SiO_2 \\ Etc.}]{\substack{Fast \\ H_2O}} \text{Products} \qquad\qquad IX$$

In the particular case of the trans isomer, cis-N_2F_2 could be formed as an intermediate. However, it is worth noting that no detectable quantities of cis-N_2F_2 were generated in any of the above reactions of the trans isomer.

As was previously noted, the effect of glass surface area on the decomposition of cis-N_2F_2 has not yet been determined.

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Colburn et al[1] reported that cis-N_2F_2 at high pressure and ambient temperature reacts completely with glass within two weeks. In contrast, experiments in this laboratory indicate that at reduced pressure no measurable decomposition occurs with either water or glass over a period of 15 hours at 60°C or several days at 25°-30°C. Thus the reported decomposition at room temperature probably proceeds via a pressure-sensitive vapor phase reaction rather than by direct attack on the glass.

REFERENCES

1.   C. B. Colburn, F. A. Johnson, ... Kennedy, K. McCallum, L. C. Metzger and C. O. Parker. JACS 81, 6397 (1959).

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